

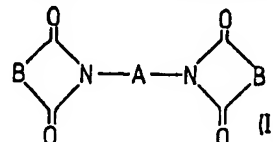
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(54) Modified thermosetting imide resins

(57) Bisimide resins having improved fracture toughness comprise a mixture of,

a) a bisimide of the general formula (I)



in which B represents a divalent radical containing a carbon-carbon double bond and A is a divalent radical containing at least two carbon atoms and

b) a polyisocyanate of the general formula (II)



in which x has a value of between 2 and 4 and D stands for an x-valent radical. The molar ratio of a:b is in the range 2 to 100.

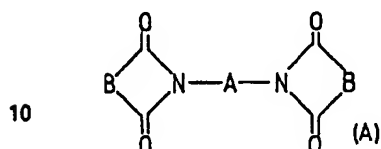
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SPECIFICATION

Modified thermosetting imide resins

5 From British Patent Specification 1066390 it is known that bisimides of the general formula (A)

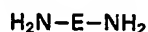
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15 In which the radical B represents a divalent organic radical containing a carbon-carbon double bond, and A represents a divalent organic radical of at least two carbon atoms, can be crosslinked by simply heating them to temperatures between 100 and 400°C, providing materials with outstanding high temperature stability. Other imide resins can be obtained according to British Patent Specification 1190718 by reacting a bisimide of the general formula (A) with a diamino compound of the general formula (B)

15

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(B)

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in which E represents a divalent organic radical of at least two carbon atoms.

25 Other examples of imide resins are obtained by reacting bisimides with dihydrazides (British Patent Application 2011920A) or amino acid hydrazides (British Patent Application 2009767A) or azomethines (British Patent Specification 1443067).

25

The so-called BI-type resins, some of which are the subjects of the above mentioned patents, are highly crosslinked when finally cured and exhibit low tensile strength, flexural strength and a low elongation at break. When these BI-type resins are used as matrix resins in crossplied graphite laminates the above mentioned combination of mechanical properties give rise to a phenomenon called "microcracks" which have a deleterious effect on the mechanical properties of the composites.

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It is an object of the present invention to provide curable bisimide resins of the BI-type which when cured lead to heat resistant tough crosslinked polymers.

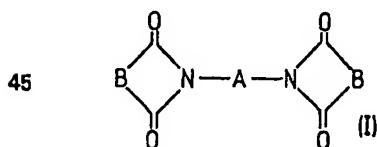
Another object of this invention is to provide BI-type curable bisimide resins which can be processed either from the melt or from the solution together with fibres like glass, graphite or aramides to form composites showing significantly reduced microcracking.

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It is a further object of this invention to provide BI-type laminating resins leading to composites with improved interlaminar fracture toughness.

The present invention relates to new and improved thermosetting imide resins which are obtained from curable bisimide resins which comprise a mixture of (a) at least one bisimide of formula I

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50 in which B is a bivalent radical containing a carbon-carbon double bond and A is a bivalent radical having at least two carbon atoms and (b) a polyisocyanate of the general formula II

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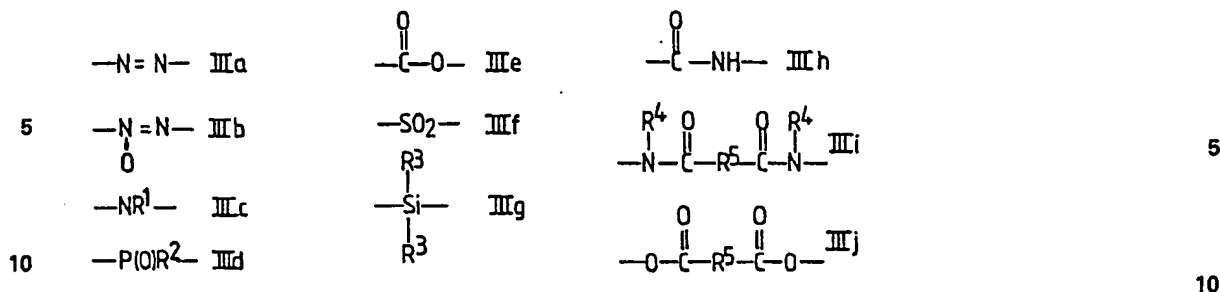
II

55 in which x has a value in the range 2 to 4 and D stands for an x-valent organic residue. The molar ratio a:b lies in the range 2 to 100. The copolymerization of bisimides with polyisocyanates can be effected by simply heating a mixture of the two to temperatures between 100 and 350°C, long enough to finalize the reaction.

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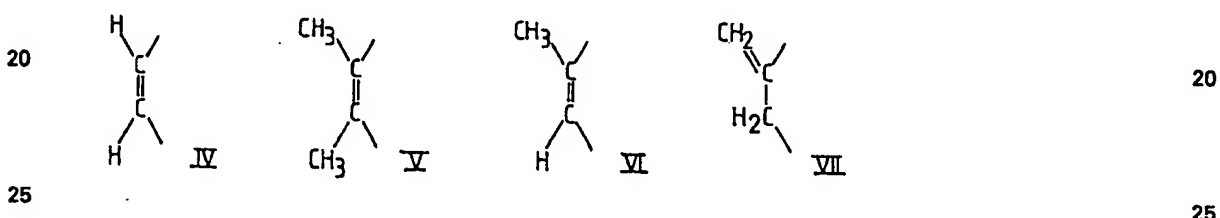
The radical designated A in general formula I may be (a) an alkylene group with up to 12 carbon atoms, (b) a cycloalkylene group with 5 to 6 carbon atoms, (c) a heterocyclic group with 4 to 5 carbon atoms and at least one nitrogen, oxygen or sulphur atom in the ring, (d) a mono or dicarbocyclic group or (e) at least two mono or dicarbocyclic aromatic or cycloalkylene groups which are connected to one another by a direct carbon-carbon bond or by a bivalent group chosen from oxygen, sulphur, alkylene with one to three carbon atoms, or a group of formula IIIa to IIIj

60



the radicals R_1, R_2, R_3, R_4 , being alkyl groups with one to five carbon atoms, R_5 being an alkylene group or an arylene group.

15 The radical B in the general formula I represents a divalent organic radical containing a carbon-carbon double bond. The radical B may have a structure as shown in formula IV, V, VI or VII 15



Bismaleimides of formula I in which the radical B is of formula IV may be used for producing the new imide resins. Examples of suitable bismaleimides are 1,2-bismaleimidoethane, 1,6-bismaleimidoethane, 1,12-bismaleimidoethane, 1,6-bismaleimido-(2,2,4-trimethyl)hexane, 1,3-bismaleimidobenzene, 1,4-bismaleimidobenzene, 4,4'-bismaleimidodiphenylmethane, 4,4'-bismaleimidodiphenylether, 4,4'-bismaleimidodiphenylsulphide, 4,4'-bismaleimidodiphenylsulphone, 4,4'-bismaleimidodicyclohexylmethane, 2,4-bismaleimidotoluene, 2,6-bismaleimidotoluene, *N,N'*-m-xylylenebismaleimide, *N,N'*-p-xylylenebismaleimide. Examples of other suitable bisimides are *N,N'*-m-phenylene-biscitraconimide and *N,N'*-4,4'-diphenylmethane-citraconimide, in which the radical B is of formula VI and *N,N'*-4,4'-diphenylmethane-bis-itaconimide in which the radical B is of formula VII. 30

The bismides of formula I may be modified with polyamines, polyhydrazides, amino acid hydrazides, azomethines or mixtures thereof. These modified bisimides are used in a similar manner to that described herein for bisimides of formula I to prepare curable bisimide resins of the present invention. 35

A wide variety of organic polyisocyanates II may be employed to react with the bisimides of the general formula I including aromatic, aliphatic and cycloaliphatic polyisocyanates, referred to here as group 1 polyisocyanates. Representative compounds include toluene-2,6-diisocyanate, toluene-2,4-diisocyanate, m-phenylenediisocyanate, 4-chloro-1,3-phenylenediisocyanate, 4,4'-biphenylenediisocyanate, 1,5-naphthylenediisocyanate, 4,4'-bisisocyanatodiphenyl methane, 2,4'-bisisocyanatodiphenylmethane, 4,4'-bisisocyanatodiphenyl ether, 4,4'-bisisocyanatodiphenylsulphide, 3,3'-bisisocyanatodiphenylsulphide, 3,3'-bisisocyanatodiphenylsulphone, 4,4'-bisisocyanatodiphenylsulphide, and aliphatic diisocyanates such as 1,4-tetramethylenediisocyanate, 1,6-hexamethylenediisocyanate, 1,10-decamethylenediisocyanate, 2,2,4-trimethylhexamethylenediisocyanate, 1,4-cyclohexylenediisocyanate, 4,4'-methylene-bis-(cyclohexylisocyanate), 1,5-tetrahydronaphthalenediisocyanate and isophoronediiisocyanate; and polyisocyanates of formula VIII 40

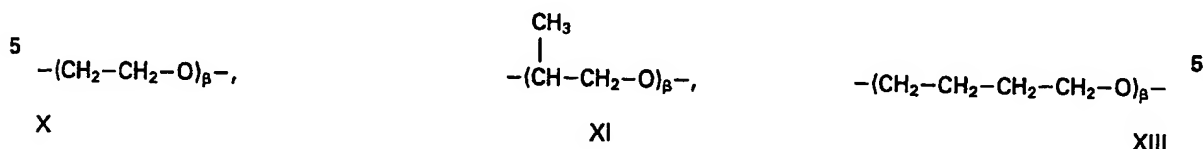


in which α has a value between 0.1 and 2 may also be employed. Very advantageous polyisocyanates to be co-reacted with bismaleimides of formula I are those obtained by the reaction of a polyisocyanate of the 60

60 the aforementioned group 1 polyisocyanates with polyalkylene ether glycols, providing isocyanate-terminated macropolyisocyanates of the formula IX, referred to here as group 2 polyisocyanates, 60



in which R represents a divalent organic aliphatic or aromatic residue and F represents a group of formula X, XI or XII



10 F representing polyalkylene ether backbone, β being a number providing glycols having molecular weights of from 200 to 10,000. The group 2 polyisocyanates of formula IX are well known substances and their preparations described in detail in *Kunststoffhandbuch*, Band VII, p. 84-85, Carl Hanser Verlag, Munchen 1966; they may be used in quantities up to 80% of the total resin mixture.

The residue F in the general formula IX can also be a polyester backbone, and the preparation of 15 polyisocyanates of formula IX with a polyester backbone is described in *Kunststoffhandbuch*, Band VII, p. 60-72, Carl Hanser Verlag, Munchen 1966.

The preparation of the new curable bisimide resins can be carried out in an inert organic solvent or diluent, for example in dimethyl formamide, dimethylacetamide, N-methyl pyrididone and tetramethyl urea, or ketone type solvents such as acetone, methyl-ethyl ketone, methyl isobutyl ketone and cyclohexanone or 20 chlorinated solvents such as methylene chloride, ethyl chloride, 1,2-dichloroethane and ether-type solvents such as dioxane, tetrahydrofuran ethyl glycol and ester type solvents such as ethyl acetate or mixed glycol ether-esters such as ethyl glycol acetate, methyl glycol acetate, diethylene glycol diethyl ether, diethylene glycol monoethyl ether acetate etc. in such a manner that prepolymer solutions are obtained. The prepolymer can be isolated by stripping off the solvent either in vacuum or by heat or both, thus providing a 25 solventless resin that can either be processed from the melt or as a powder.

The preparation of the new curable bisimide resins can be performed by using conventional techniques for mixing and grinding of powders or powders and liquids to intimately blend the bismaleimides with the polyisocyanates. Prepolymers are obtained by heating the homogeneous mixture at a temperature between 80 and 200°C, for sufficient time to produce a still formable and soluble product.

30 The production of the new curable bisimide resins according to this invention can also be carried out in inert diluents in which either only one of the starting materials is completely soluble or all the starting components are completely soluble. The latter procedure is preferred when the application of the resin requires a solution as is the case for the production of prepreps.

For many industrial applications of the new curable bisimide resins of the present invention, it is 35 advantageous to accelerate the curing process by adding catalysts. Effective curing catalysts are organic peroxides such as ditertiary butyl peroxide, diamyl peroxide, t-butyl perbenzoate in the concentration of 0.05 to 0.5% in relation to the total weight of the curable bisimide resin. Other catalysts that may be used are tertiary amines like N,N'-dimethylaniline, N,N'-dimethyl-benzylamine, N-methylmorpholine, tri-n-butylamine, tri-methylamine and azabicyclooctane and others.

40 The catalysts can be admixed with the components of the curable bisimide resins or they may be added during the production of the prepolymers either by a powder blending process or by the solvent blending process described above.

In many cases it is necessary to process the new curable bisimide resins of the present invention from the melt. To reduce the melt viscosity and to improve the pot life the resins can be blended with so-called 45 reactive diluents, preferably those that are liquid at room temperature. The reactive diluents that may be employed carry one or more polymerizable double bonds of the general formula XIII



and may be of the vinyl-, allyl- or acryl- type. These reactive diluents can be of the ether, ester, hydrocarbon or heterocyclic type. Typical ethers that may be employed are vinylallylether, diallylether, methallylether and vinylphenylether. Typical esters are vinyl-, allyl- methylallyl-, 1-chlorallyl-, crotyl-, isopropenyl esters derived 55 from saturated or unsaturated aliphatic or aromatic mono- or polycarboxylic acids such as formic, acetic, propionic, butyric, oxalic, malonic, adipic, sebacic, acrylic, methacrylic, phenylacrylic, crotonic, maleic, fumaric, itaconic, citraconic, tetrahydrophthalic, benzoic, phenylacetic, o-phthalic, isophthalic or terephthalic acid and naphthalic-dicarboxylic acid or mixtures thereof. The most important hydrocarbon type reactive diluents to be used are styrene, methylstyrene, vinylhexane, vinylcyclohexane, divinylbenzene, divinyl 60 cyclohexane, diallylbenzene, vinyltoluene and 1-vinyl-4-ethyl-benzene or mixtures thereof. Examples of heterocyclic type reactive diluents are vinylpyridine and vinylpyrrolidine.

In those cases where reactive diluents are used it is possible to first blend the bisimide components with the reactive diluent and then the polyisocyanate component is added. In those cases where the polyisocyanates of the group 2 are used to modify the bisimide resins the polyisocyanate is preferably 65 dissolved in the reactive diluent and then blended with the bismaleimide compounds. The quantity of

reactive diluent that may be employed can be up to 80% by weight of the total final resin mixture.

Very advantageous reactive diluents are styrene and divinylbenzene which are used in quantities up to 30% of the total bisimide-polyisocyanate mixture. Care has to be taken with these diluents because they crosslink at very low temperatures, at around 100-110°C, therefore mixtures containing these diluents have to be prepared at temperatures well below 100°C.

The new curable bisimide resins of the present invention can be further modified with unsaturated polyester resins. Useful unsaturated polyesters are well known products which are prepared by polycondensation of polycarboxylic acid derivatives such as esters with polyglycols as described in detail in *Kunststoffhandbuch*, Band VII, p. 247-282, Carl Hanser Verlag, München 1973.

Solutions of these polyesters in the reactive diluents described above can be used instead of the reactive diluent alone to modify the new bisimidepolyisocyanate resins.

The new curable bisimide resins of the present invention either modified or not can be thermally converted to crosslinked polyimide-isocyanate copolymers by heating them to temperatures of between 100 and 400°C, for a time sufficient to complete cure.

The new curable bisimide resins are advantageously used to produce laminated materials. In such a case the prepolymers produced from the curable bisimide resins are dissolved in suitable solvents to provide a 50-60% by weight solution, which is used to impregnate glass fibres in the form of fabrics or rovings or carbon fibres or boron fibres or organic synthetic fibres in the form of fabrics, filaments or rovings are impregnated with this solution and then stripped of the solvent by drying after which they are moulded into laminate form by the application of pressure and temperature, the crosslinked polyimide-isocyanate copolymer being the binder.

The curable bisimide resins according to the invention can also be processed by the known methods of the powder moulding industry in relation to curable compositions, to produce mouldings, curing out taking place with simultaneous shaping under pressure. For these applications it is possible to admix with the curable bisimide resins additives such as fillers, colourants, softeners and flameproofing agents. Ideal fillers are for example glass fibres, carbon fibres, organic high modulus fibres such as aramides, quartz flour, kaolin, silica and metals in the form of fine powders.

It is possible to modify the heat-resistance, flexibility and toughness of the resins by varying the molar proportions of the bismaleimides and the polyisocyanates over a whole range, and furthermore mixtures of two or more bismaleimides may also be used.

Accordingly, the following examples are selected to demonstrate the advantageous utility of the new resins and compositions but are not limited to them.

Example 1

100 g of 4,4'-bismaleimidodiphenylmethane, 40 g of (2,4-2,6)-bismaleimidotoluene and 20 g of 4,4'-diisocyanatodiphenylmethane were mixed intimately by use of a ball mill. The mixture thus obtained was heated to 145°C, providing a viscous melt which was processed as follows:

(a) The molten mixture of the reactants was poured into a casting mould measuring 100 × 100 × 3 mm to form a plate which was hardened over two hours at 170°C, and for an additional 3 hours at 200°C. After removal from the mould the plate was postcured for 15 hours at 250°C. The plate was then cut into test pieces (40 × 10 × 3 mm) and tested according to DIN 53452 in a three point flexured test. The flexural strength obtained was 90 N/mm², the flexural modulus was 4.8 KN/mm². After 1000 hours ageing in circulating air at 220°C the remaining properties were:

flexural strength	92 N/mm ²
flexural modulus	4.8 KN/mm ²

indicating extremely good thermal oxidative stability.

(b) The molten mixture of the reactants was heated for 1 hour at 180°C thus providing after grinding a prepolymer powder which was cured in a cylindrical mould at a temperature of 180-220°C. The moulding pressure necessary to obtain a dense void free specimen was 300-500 N/mm². The flexural strength of the moulding measured was 120 N/mm²; the flexural modulus was found to be 4600 N/mm².

(c) The intimate mixture of 4,4'-bismaleimidodiphenylmethane, (2,4-2,6)-bismaleimidotoluene and 4,4'-diisocyanatodiphenylmethane obtained by ball milling as described above was dissolved in methylene chloride-ethylglycol acetate mixture as a solvent to form a low viscosity solution containing 60% by weight of resin. This solution was used to impregnate glass fabric type 92111/A1100 of Messrs. Interglas, thus providing after stripping off the solvent in a circulating air oven at 100°C, for ten minutes, a prepreg containing 35 to 37% by weight of resin. The prepreg pieces were stacked in a heated platen press and cured at 200°C for 4 hours, providing a laminate in which the crosslinked polyimide-isocyanate copolymer was the binder. After postcure at 250°C, the laminate showed the following properties.

	Fibre content	65%	
	Resin content	35% by weight	
5	Density	1.95 g/cm ³	5
	Flexural Strength at room temperature	590 N/mm ²	
	Flexural Strength at 250°C	410 N/mm ²	
10	Flexural Modulus at room temperature	28 KN/mm ²	10
	Flexural Modulus at 250°C	24 KN/mm ²	
15	Short beam shear strength	51 N/mm ²	15
	Short beam shear strength at 250°C	38 N/mm ²	

Example 2

- 20 56 g of 4,4'-bismaleimidodiphenylmethane, 24 g of 2,4-bismaleimidotoluene and 20 g of 2,2,4-tri-
methylhexamethylenebismaleimide were melted in a round bottomed flask at 150°C and degassed to form a
clear transparent melt. The melt thus obtained was dissolved in methylene chloride at room temperature
and blended with 40 g of a 50% by weight solution of 2,4-2,6-diisocyanatotoluene in methylene chloride, also
containing 20 g of divinyl benzene. The mixture was heated progressively to a temperature of 75°C, finally a
25 vacuum was used to strip off traces of solvent, thus providing a resin that could be processed according to
Example 1, employing the melt casting technology. 25

Example 3

- A resin according to British Patent Application 2009767A, Example 1 was produced by blending 107.5 g
30 (0.3 mols) of 4,4-bismaleimidodiphenylmethane and 18.12 g (0.12 mols) m-aminobenzoic acid hydrazide in a
ball mill after which the mixture was prereacted for 35 minutes in a drying cabinet at a temperature of 150°C.
The homogeneous melt thus obtained was dissolved in N-methylpyrrolidone to form a 50% by weight
solution. This solution was blended with 4,4'-diisocyanatodiphenylmethane (0.1 mols) and used to produce
glass fabric prepregs. Prepregs thus obtained were moulded at a pressure of 500 n/mm² at 200°C for 4 hours
35 to produce a laminate in which the new crosslinked polyimide-isocyanate copolymer was the binder. 35

Example 4

- A resin according to British Patent Application 2009767A was produced by blending 56 g of
bismaleimidodiphenylmethane, 24 g of bismaleimidotoluene (2,4- and 2,6- isomeric mixture) and 10 g
40 m-aminobenzoic acid hydrazide. To this resin a solution of 5 g of the macroisocyanate (mi) in 10 g
diallylphthalate was added and heated to 110°C while stirring, to form a highly viscous melt which was cast
into a parallel epipedic mould and cured under a pressure of 2 bars for 12 hours at 180°C. After demoulding,
the casting was postcured for 15 hours at 250°C, providing a resin sample containing no filler with the
following properties:

45		RT	250°C	45
	Density	1.26 g/cm ³	-	
50	Flexural Strength	110 N/mm ²	65 N/mm ²	50
	Flexural Modulus	4.6 KN/mm ²	2.9 KN/mm ²	
55	Flexural Strength after 1000 hours at 200°C	115 N/mm ²	58 N/mm ²	55
	Flexural Modulus after 1000 hours at 200°C	4.65 KN/mm ²	3.1 KN/mm ²	

- 60 Preparation of the macroisocyanate (mi) 60
350 g of 4,4' diisocyanatodiphenylmethane and 821 g of tetramethylene glycol (molecular weight 1000)
were stirred and heated in a round bottomed flask under nitrogen gas at a temperature of 85°C for 1.5 hours,
providing a macroisocyanate showing an isocyanate content of 1×10^{-3} mols. g⁻¹.

Example 5

A resin consisting of 60 parts of 4,4'-bismaleimidodiphenylmethane, 20 parts of toluene bismaleimide, 15 parts of 2,2,4-trimethylhexamethylene bismaleimide and 10 parts of 4,4'-diisocyanatodiphenylmethane was prepared by melt blending at a temperature of 125°C. To this melt 15 parts of the polyester sold under the trade name Dobekan FT1018 by Bech & Co., Hamburg, dissolved in 15 parts of divinylbenzene were added and intimately mixed at 70-80°C for 15 minutes providing a resin melt which was cast into a parallel epipedic form and cured under pressure for 15 hours at 200°C. After postcure at 250°C, for 15 hours the casting showed the following properties.

10	RT	250°C	10
	Density (g/cm ³)	1.27	
	Flexural Strength (N/mm ²)	105	79
15	Flexural Modulus (KN/mm ²)	4.1	2.7
	Flexural Strength (N/mm ²) after 250 hours at 300°C	80	46
20	Flexural Modulus (KN/mm ²) after 250 hours at 300°C	4.6	3.2

Example 6

A resin consisting of 60 parts of 4,4'-bismaleimidodiphenylmethane, 20 parts of toluenebismaleimide, 20 parts of 4,4'-diisocyanatodiphenylmethane was prepared by melt blending at a temperature of 120°C. This melt was cooled down to a temperature of 70°C, blended with 15 parts of a solution of the macroisocyanate (mi) of Example 4 in divinylbenzene (1:2), providing a low viscosity melt at 80°C. This resin could be processed from the melt as described in Example 1, or can be dissolved in methylenechloride to form an impregnation varnish which was used to impregnate glass fabric squares (15 × 15 cm) which after drying in a circulating air oven at 40-50°C for 20 minutes provide glass fabric prepreps which contain 40% by weight of resin. These prepreps were stacked in a heated platen press between aluminium foils and cured at 170°C for 2 hours at a pressure of 60 N/cm². The laminate thus obtained was postcured in a circulating air oven at a temperature of 250°C for 16 hours. The laminate obtained showed the following properties:

35	Resin content	30% by weight	35
	Density	1.95 g/cm ³	
40	Flexural Strength at RT	640 N/mm ²	40
	Flexural Strength at 250°C	380 N/mm ²	
	Flexural Modulus at RT	29.5 KN/mm ²	
45	Flexural Modulus at 250°C	21.0 KN/mm ²	45
	Short beam shear strength at RT	58 N/mm ²	
50	Short beam shear strength at 250°C	41 N/mm ²	50

Example 7

A resin consisting of 56 parts of 4,4'-bismaleimidodiphenylmethane, 24 parts of 2,4-bismaleimidotoluene and 40 parts of a styrene solution of the unsaturated polyester sold under the trade name Dobekan FT 1018 (1:1) was prepared by melting the components at 70-80°C. After cooling the resin was dissolved in 120 parts of methylene chloride to which a solution of 5 parts of the macroisocyanate (mi) of Example 4 dissolved in 10 parts of methylene chloride was added under stirring to provide a homogeneous resin solution. Methylene chloride was stripped off in vacuum by use of a rotary evaporator and the final melt thus obtained was degassed in vacuum of 70-75°C. The resin melt could be further processed as described in Example 1.

Example 8

A resin consisting of 56 parts 4,4'-bismaleimidodiphenylmethane, 24 parts of 2,4-bismaleimidotoluene, 20 parts of 4,4'-diisocyanatodiphenylmethane, and 30 parts of the unsaturated polyester sold under the trade name Dobekan FT 1018 were melt blended at 110°C for 15 minutes, said melt being mixed with a solution of 0.7 parts of azobicyclooctane dissolved in 30 parts of diallylphthalate at a temperature of 70-100°C. The resin

thus obtained was processed as follows:

(a) The molten mixture prepared as described above was poured into a mould as described in Example 1 and cured for 2 hours at 170°C, and 2 hours at 200°C. After demoulding the plate is postcured at 210°C for 15 hours. The following properties were obtained.

5	Flexural strength at 25°C	105 N/mm ²	5
	Flexural strength at 250°C	49 N/mm ²	
10	(b) The molten mixture of the reactants was heated for 1 hour at 164°C thus providing after grinding, a prepolymer which was cured in a cylindrical mould at temperatures of between 170-210°C, and at pressures of 250-400 N/cm ² .		10
15	(c) 100 parts of the resin mixture prepared as described above was dissolved in 60 parts of acetone to form a low viscosity resin solution which was used to impregnate carbon fibre rovings (type Celion 6000) and carbon fibre unidirectional tapes were measured by a filament winding operation. The tapes were dried at 30°C in circulating air and moulded in an autoclave at a pressure of 6 bars for 3 hours at 170°C. The unidirectional laminate obtained was postcured for 15 hours at 210°C and showed the following properties:		15
20	Density	1.50 g/cm ³	20
	Flexural Strength at 25°C	2050 N/mm ²	
	Flexural Strength at 250°C	1350 N/mm ²	
25	Flexural Modulus at 25°C	128 KN/mm ²	25
	Flexural Modulus at 250°C	124 KN/mm ²	
30	Interlaminar shear strength at 25°C	95 N/mm ²	30
	Interlaminar shear strength at 250°C	52 N/mm ²	

CLAIMS

- 35 1. Curable bisimide resins comprising a mixture of
a) at least one bisimide of the general formula I 35

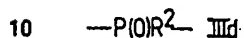
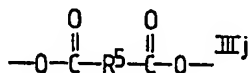
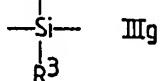
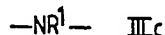
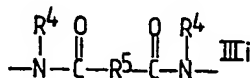
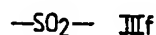
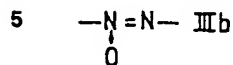
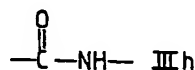
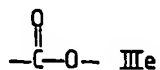
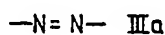


- 45 in which B represents a divalent radical containing a carbon-carbon double bond and A is a divalent radical containing at least two carbon atoms and
b) a polyisocyanate of the general formula (II) 45



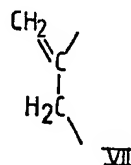
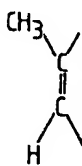
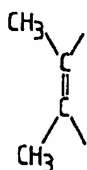
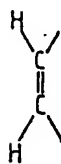
In which x has a value in the range 2 to 4 and D stands for an x-valent radical,
in which the molar ratio a:b is in the range 2 to 100.

- 55 2. Curable bisimide resins according to claim 1 in which the bisimide of the general formula I is characterised in that 55
- A being a member selected from the groups consisting of (a) an alkylene group with up to 12 carbon atoms, (b) a cycloalkylene group with 5 to 6 carbon atoms, (c) a heterocyclic group with 4 to 5 carbon atoms and at least one nitrogen, oxygen or sulphur atom in the ring, (d) a mono or dicarbocyclic group or (e) at least two mono or dicarbocyclic aromatic or cycloalkylene groups which are connected to one another by a direct carbon-carbon bond or by a bivalent group chosen from oxygen, sulphur, alkylene with one to three carbon atoms, or a group of formulae IIIa to IIIj 60



the radicals R_1, R_2, R_3, R_4 , being alkyl groups with one to five carbon atoms, R_5 being an alkylene group or an arylene group and

15 - B is a group which is capable of addition polymerization selected from a group of formula IV, V, VI or VII



3. Curable bisimide resins as claimed in claim 1 or claim 2 in which the polyisocyanate of the general formula II is selected from one of the following compounds:

toluene 2,6-diisocyanate,

toluene 2,4-diisocyanate,

m-phenylenediisocyanate,

4-chloro 1,3-phenylenediisocyanate,

4,4'-biphenylenediisocyanate,

1,5-naphthylenediisocyanate,

4,4'-bisisocyanatodiphenylmethane,

2,4'-bisisocyanatodiphenylmethane,

4,4'-bisisocyanatodiphenyl ether,

4,4'-bisisocyanatodiphenylsulphone,

3,3'-diisocyanatodiphenylsulphone,

4,4'-bisisocyanatodiphenylsulphide,

1,4-tetramethylenediisocyanate,

1,6-hexamethylenediisocyanate,

1,10-decamethylenediisocyanate,

2,2,4-trimethylhexamethylenediisocyanate

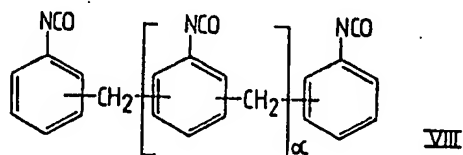
1,4-cyclohexylenediisocyanate,

4,4'-methylene-bis-(cyclohexylisocyanate),

1,5-tetrahydronaphthalenediisocyanate,

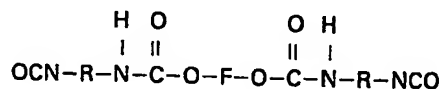
isophorone diisocyanate,

or a polyisocyanate of formula VIII



in which α has a value of between 0.1 and 2.

4. Curable bisimide resins as claimed in claim 1 or claim 2 in which the polyisocyanate of the general formula II is a diisocyanate of the formula IX



IX

in which R represents a divalent organic residue and F stands for a divalent polyalkylene ether glycol of formula X, XI or XII



β being a number providing a molecular weight for the structure (IX) of between 200 and 10,000.

15 5. Curable bisimide resins as claimed in claim 4 wherein the diisocyanate IX is present in quantities up to 80% of the total final resin mixture by weight. 15

6. Curable bisimide resins as claimed in any one of claims 1 to 5 containing a reactive diluent which carries at least one polymerizable double bond of the general formula XIII



25 which may be of the vinyl-, allyl-, or acryl- type. 25

7. Curable bisimide resins as claimed in claim 6 in which the reactive diluent is one of the following compounds or mixtures thereof: styrene, methylstyrene, vinyltoluene, divinylbenzene, vinylcyclohexane, divinylcyclohexane, vinylpyridine, vinylpyrrolidone.

8. Curable bisimide resins as claimed in claim 7 wherein the reactive diluent is present in quantities up to 80% of the total final resin mixture by weight. 30

9. Curable bisimide resins as claimed in claim 8 wherein the reactive diluent is styrene or divinylbenzene, the reactive diluent being present in quantities up to 30% of the total final resin mixture by weight.

10. Curable bisimide resins as claimed in any one of claims 1 to 9 characterized by containing an unsaturated polyester, the said unsaturated polyester being obtained by the polycondensation of polycarboxylic acids with polyglycols. 35

11. Curable bisimide resins as claimed in any one of claims 1 to 10 in which the bisimide of the general formula (I) is modified with compounds selected from one of the following groups: polyamines, polyhydrazides, amino acid hydrazides, azomethines, or mixtures thereof.

12. Curable bisimide resins as claimed in any one of claims 1 to 11 containing curing catalyst selected from one of the following compounds: 40

ditertiary butyl peroxide,
diamyl peroxide,
t-butyl perbenzoate,
N,N' dimethylbenzylamine,
N,N' dimethyl aniline,
N-methylmorpholine,
tri-n-butylamine,
tri-methylamine and
azabicyclooctane.

13. Curable bisimide resins as claimed in claim 12 wherein a peroxide catalyst is present in the concentration of 0.05 to 0.5% of the total final resin mixture by weight. 50

14. Prepolymers obtained by heating the curable bisimide resins as claimed in any one of claims 1 to 13 to temperatures of between 80 and 200°C for a time sufficient to obtain a still formable product.

15. Prepolymers as claimed in claim 14 wherein a catalyst is used and the resin mixture is in the melt form or in solution. 55

16. Solutions of curable bisimide resins as claimed in any one of claims 1 to 15 in an inert organic solvent selected from dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, tetramethyl urea, acetone, methyl-ethyl ketone, methyl-isobutyl ketone, cyclohexanone, methylene chloride, ethyl chloride, 1,2-dichloroethane, dioxane, tetrahydrofuran, ethyl glycol, ethyl acetate, ethyl glycol acetate, methyl glycol acetate, diethyleneglycol diethyl ether, diethyleneglycol monoethyl ether acetate and mixtures thereof. 60

17. Solutions according to claim 16 suitable for producing laminates in which the resin is present in a concentration of 50 to 60% of the solution by weight.

18. Crosslinked polyimide-isocyanate copolymers derived by heating the curable bisimide resins mixtures of claims 1 to 12 to temperatures of between 80 and 400°C for a time sufficient to complete cure.

19. Crosslinked polyimide-isocyanate copolymers derived by heating the prepolymers of claims 14 and 65

- 15 to temperatures of between 80 and 400°C for a time sufficient to complete cure.
20. Fibrous materials impregnated with curable bisimide resins as claimed in claims 1 to 13, prepolymers as claimed in claim 14 or 15 or solutions as claimed in claims 16 or 17.
21. Impregnated materials as claimed in claim 20 in which the fibrous materials are rovings, fabrics, mats
5 or felts.
22. Articles formed under heat and pressure from the curable bisimide resins claimed in claims 1 to 13. 5
23. Articles formed under heat and pressure from the prepolymers claimed in claims 14 and 15.
24. Articles formed under heat and pressure from the impregnated fibrous materials as claimed in claim 20 or 21.

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